

Statistical Thermodynamics in Chemistry and Biology

7. The logic of thermodynamics

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Some key concepts in classical thermodynamics

- ▶ First law of thermodynamics
- ▶ Quasi-static processes
- ▶ Heat capacity
- ▶ Thermodynamic cycles

The first law interrelates heat, work and energy

- ▶ **First law of thermodynamics:**

$$dU = \delta q + \delta w$$

- ▶ δq and δw are path-dependent properties (not state variables)
- ▶ dU is a state function,

$$\Delta U = \int_A^B dU = U_B - U_A$$

so ΔU depends only on the start state and the end state (not on the path).

- ▶ The first law is defined so that
 - ▶ $\delta q > 0$ when heat flows **into** the system.
 - ▶ $\delta w > 0$ when work is done **on** a system.

Quasi-static processes

- ▶ Thermodynamics is about equilibrium, not about rates (see irreversible thermodynamics, see transport processes in chap. 17).
- ▶ Processes are **quasi-static** if they are performed slowly enough that their properties are independent of time and independent of the speed of the process.
- ▶ For a gas in a chamber where work is carried out by a piston, a **quasi-static** process is defined as

$$\delta w = -p_{\text{ext}} dV$$

The heat capacity, C_V

- ▶ Measuring the heat capacity in a bomb calorimeter: fixed volume

$$\delta w = -p_{\text{ext}}dV = 0$$

leading to for $U(S, V, N)$ and ignoring terms in N ,

$$dU = \delta q = TdS$$

- ▶ The heat capacity, C_V , is defined as the amount of heat needed to raise the temperature of the system with 1 K at constant V :

$$C_V = \left(\frac{\delta q}{dT} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

- ▶ If we know the temperature dependence of C_V :

$$dU = C_V dT \quad \Rightarrow \quad \Delta U = \int_{T_A}^{T_B} C_V(T) dT$$

- ▶ Similar expression at constant pressure in chapter 8: C_p

Heat capacities of gases

- ▶ Regard $U(V, T)$ for a gas,

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

- ▶ For a gas, the dependence of U on V can be ignored,

$$\left(\frac{\partial U}{\partial V} \right)_T \approx 0$$

since the gases are dilute and rarely interact.

- ▶ So whether **we have constant volume or not**,

$$dU = C_V dT \quad (\text{for a gas at low density})$$

Reversible processes

- ▶ A process is called **reversible** if returning the system to its initial conditions also returns the surroundings to its initial conditions (no conversion of energy that cannot be recaptured).
- ▶ We can relate (for a closed system, $dN = 0$):

$$dU = TdS - pdV = \delta q + \delta w$$

In a quasi-static process: $\delta w = -pdV$, which leads to

$$dS = \frac{\delta q_{\text{rev}}}{T}$$

- ▶ This is often referred to as the **thermodynamic definition of entropy**.
- ▶ Also since (for $dV = dN = 0$),

$$dU = TdS = C_V dT \quad \Rightarrow \quad \Delta S = \int_A^B dS = \int_{T_A}^{T_B} \frac{C_V}{T} dT$$

Thermodynamic cycles and fictitious processes

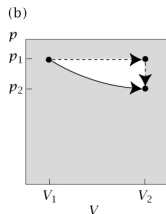
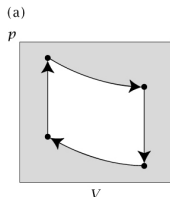
- ▶ Changes in **state variables**, like p , V , T , N , U and S , do not depend on the path, e.g. $\Delta U = U_2 - U_1$ only depends on the start and end states.
- ▶ Heat and work are **not** state variables.
- ▶ For example, you can introduce a **fictitious** state A ,

$$\Delta U = (U_2 - U_A) + (U_A - U_1)$$

which may simplify the problem dramatically.

Right figure below: The process is divided into two parts, one with constant pressure and one with constant volume.

- ▶ Similarly, **thermodynamic cycles** (left figure below) can be utilized since $\Delta U = 0$ for the entire process (all the way around).



Four processes to describe an ideal gas

- **Constant-volume (isochoric) process:** $(p_1, V_0, T_1) \rightarrow (p_2, V_0, T_2)$
no volume change gives $p dV = 0$,

$$\Delta U = q = \int_{T_1}^{T_2} C_V(T) dT$$

- **Constant-pressure (isobaric) process:** $(p_{\text{ext}}, V_1, T_1) \rightarrow (p_{\text{ext}}, V_2, T_2)$

$$w = - \int_{V_1}^{V_2} p_{\text{ext}} dV = -p_{\text{ext}} (V_2 - V_1)$$

- We have (recall, also when the volume is not constant),

$$\Delta U = \int_{T_1}^{T_2} C_V dT$$

so that $q = \Delta U - w$.

Four processes to describe an ideal gas

Part 2

- **Constant-temperature (isothermal) process:** $(p_1, V_1, T_0) \rightarrow (p_2, V_2, T_0)$
in this case, it is assumed that $p_{\text{int}} = p_{\text{ext}}$ in a quasistatic process (slow enough for the internal pressure to adapt to the external pressure):

$$w = - \int_{V_1}^{V_2} p_{\text{ext}} dV = - \int_{V_1}^{V_2} p_{\text{int}} dV = - \int_{V_1}^{V_2} \frac{Nk_B T}{V} dV = -Nk_B T \ln \frac{V_2}{V_1}$$

where we in the last steps have assumed an ideal gas.

- At constant temperature, $dU = C_V dT = 0$, so that $q = -w$ since $\Delta U = w + q$.

Four processes to describe an ideal gas

Part 3

- ▶ **Adiabatic process:** $(p_1, V_1, T_1) \rightarrow (p_2, V_2, T_2)$

- ▶ Definition of adiabatic process: $\delta q = 0$.

- ▶ We use

$$C_V dT = dU = -pdV$$

- ▶ For an ideal gas,

$$C_V dT = -\frac{Nk_B T}{V} dV$$

- ▶ Rearrange and integrate,

$$\int_{T_1}^{T_2} \frac{C_V}{T} dT = - \int_{V_1}^{V_2} \frac{Nk_B}{V} dV \quad \Rightarrow \quad C_V \ln \frac{T_2}{T_1} = -Nk_B \ln \frac{V_2}{V_1}$$

where we in the last term assumed that C_V is independent of the temperature.

Heat engine: Carnot cycle

- Heat engine: take in heat and perform work

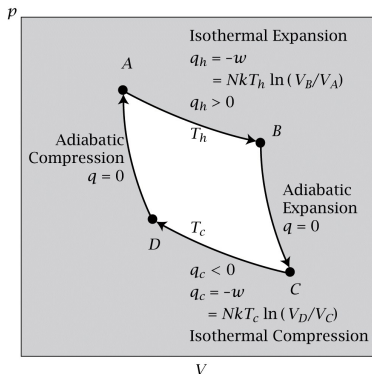


Figure 7.5 Molecular Driving Forces 2/e (© Garland Science 2011)

Heat engine: Carnot cycle

Part 2

- ▶ Two adiabatic and two isothermal steps (at T_h and T_c).
- ▶ $dU = 0$ for the entire process (thermodynamic cycle), so $q_{\text{tot}} = -w_{\text{tot}}$.
- ▶ For the two adiabatic steps: $q = 0$.
- ▶ For the two isothermal steps: $q = -w$,

$$q_{\text{tot}} = q_h + q_c = Nk_B T_h \ln \frac{V_B}{V_A} + Nk_B T_c \ln \frac{V_D}{V_C}$$

- ▶ To simplify use the adiabatic steps,

$$\frac{V_C}{V_B} = \left(\frac{T_h}{T_c} \right)^{\frac{C_V}{Nk_B}} = \frac{V_D}{V_A} \quad \Rightarrow \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

which gives

$$w_{\text{tot}} = -q_{\text{tot}} = -Nk_B (T_h - T_c) \ln \frac{V_B}{V_A}$$

The Carnot cycle is reversible

- Demonstrate by showing,

$$\Delta S = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA} = 0$$

- For the two adiabatic steps:

$$\Delta S_{\text{adiabatic}} = \frac{q}{T} = 0$$

- For the isothermal steps,

$$\Delta S_{AB} = \frac{q_h}{T_h} = Nk_B \ln \frac{V_B}{V_A}$$

and

$$\Delta S_{CD} = \frac{q_c}{T_c} = Nk_B \ln \frac{V_A}{V_B} \quad \text{since} \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

- Summing these terms gives 0.

Why do engines waste heat?

- Consider the following three steps of the cycle:

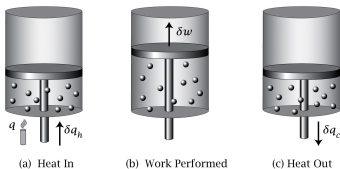


Figure 7.4 Molecular Driving Forces 2/e (© Garland Science 2015)

- ΔU is a state function,

$$w = q_h - q_c$$

- Define the efficiency as

$$\eta = \frac{w}{q_h} = 1 - \frac{q_c}{q_h}$$

- For a reversible process,

$$\Delta S_{\text{total}} = \Delta S_h + \Delta S_c = \frac{q_h}{T_h} - \frac{q_c}{T_c} = 0$$

- Rearrange,

$$\frac{q_c}{q_h} = \frac{T_c}{T_h} \quad \Rightarrow \quad \eta = 1 - \frac{T_c}{T_h}$$